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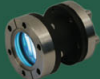



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Tuning of silicene-substrate interactions with potassium adsorption

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The evolution of the electronic structure and the structural stability of epitaxial silicene on ZrB₂(0001) thin films exposed to K atoms has been studied by angle-resolved photoelectron spectroscopy and low-energy electron diffraction. Potassium adsorption leads to charge donation to the silicene lattice, which is accompanied by the partial filling of a formerly unoccupied π^* band and by the increasing hybridization between the diboride surface state and the lower branch of the back-folded π band. The results allow an identification of silicene-derived π electronic states and confirm that before K adsorption, the interactions at the silicene-substrate interface are rather weak.

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A single atom thick honeycomb structure made of Si atoms—silicene—is attracting a lot of interest due to its graphene-like electronic structure,^{1–3} the occurrence of a large quantum spin Hall effect,^{4,5} and a topological quantum phase transition;⁶ properties that are theoretically predicted for its free-standing form. Although chemical exfoliation of silicon sheets from calcium disilicide has been demonstrated,⁷ the synthesis of free-standing silicene remains a major challenge. On the other hand, epitaxial silicene sheets have recently been prepared on both Ag(111)^{8–11} and ZrB₂(0001)¹² surfaces. Due to the interactions with the respective substrates, these sheets possess crystal and electronic structures different from free-standing silicene^{10,12} and also from each other. Epitaxial silicene on the ZrB₂(0001) surface has an in-plane lattice constant of about 3.65 Å, shows a particular atomistic buckling and is ($\sqrt{3} \times \sqrt{3}$)-reconstructed.¹² Here, we report on the results of an experimental study aimed to shed light on the interactions between silicene and the diboride substrate. The reaction of silicene with strong electron donors like potassium atoms could provide insight into the nature of electronic states close to the Fermi level, E_F , as predicted by theory^{13–15} and as it does for graphite (0001),¹⁶ graphene,^{17,18} and Si(111)-(7 × 7)^{19,20} surfaces. In particular, recent calculations describing the K adsorption characteristics on buckled, free-standing silicene^{14,15} find that K atoms adsorb preferentially on hollow sites. The predicted ionic interaction is stronger than that of potassium atoms with graphene¹⁴ and results in a filling of unoccupied π bands in the vicinity of the K point such that bands appear to be almost rigidly shifted towards higher binding energy.¹⁵ This renders semi-metallic silicene metallic.^{14,15}

Single-crystalline zirconium diboride (ZrB₂) thin films were grown by ultrahigh vacuum (UHV) chemical vapour epitaxy, as described elsewhere.²¹ Following the *ex situ* transfer to measurement set-ups, native oxide was removed by annealing at about 1050 K for 12 h under UHV conditions with a pressure better than 5×10^{-9} mbar. During this procedure, a well-defined silicene layer is formed by surface

segregation on the outermost Zr layer of the ZrB₂(0001) thin film, which appears as a (2 × 2)-reconstructed ZrB₂(0001) surface.¹² The samples were exposed to K vapor from well-degassed getter sources (ALVASOURCE, Alvatec Alkali Vacuum Technologies GmbH) with the substrates held at room temperature. For the calibration of the rate, the change of the work function, $\Delta\phi$, as a function of the amount of potassium was measured following the stepwise deposition of K atoms onto the Si(111)-(7 × 7) surface.²⁰ The work function, ϕ , was derived from the cut-off of the secondary electron spectra taken at two set-ups, the Spectroscopic Low-Electron Energy Microscopy (Elmitec SPE-LEEM) end-station located at BL U5UA of the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory (BNL), Upton, NY, USA),²² the sample excited at $h\nu = 43$ eV, and separately using the SES-100 hemispherical analyzer at BL-18A of the Photon Factory (PF) synchrotron radiation facility located at the High-Energy Accelerator Research Organization (KEK, Tsukuba, Japan).²⁰ Angle-resolved valence band photoelectron (ARPES) spectra were recorded with the latter set-up using the photon energy of $h\nu = 43$ eV. The total energy resolution was better than 130 meV. Microspot low-energy electron diffraction (μ -LEED) patterns were obtained with the LEEM set-up using the kinetic energy of 30 eV.

Figure 1 shows a comparison of the change of the work function, $\Delta\phi$, between the Si(111) and silicene on ZrB₂(0001) surfaces at room temperature as a function of the K/Si ratio x , as measured at NSLS-BL U5UA. In order to calibrate the x scale, the K/Si(111) data have been compared to the reduction of the work function in the Si(111) δ (7 × 7) data published by Sakamoto *et al.*²⁰ According to the saturation behaviour and within relatively large error bars, a value of x of about $\Delta\phi = -2.3$ eV can then be related to $x = 0.33 \pm 0.05$, defined as 1/3 of a monolayer.²⁰ For the work function data measured at KEK-PF BL-18A, the x scale was re-normalized to match the curve obtained at the other set-up.

For silicene on ZrB₂(0001) and for at least at $x < 0.6$, the original ϕ of 4.61 ± 0.16 eV (Ref. 21) is reduced by an amount smaller than that observed on the Si(111) surface: First, at about $x = 0.2$, $\Delta\phi$ levels at a value of about -1.2 eV.

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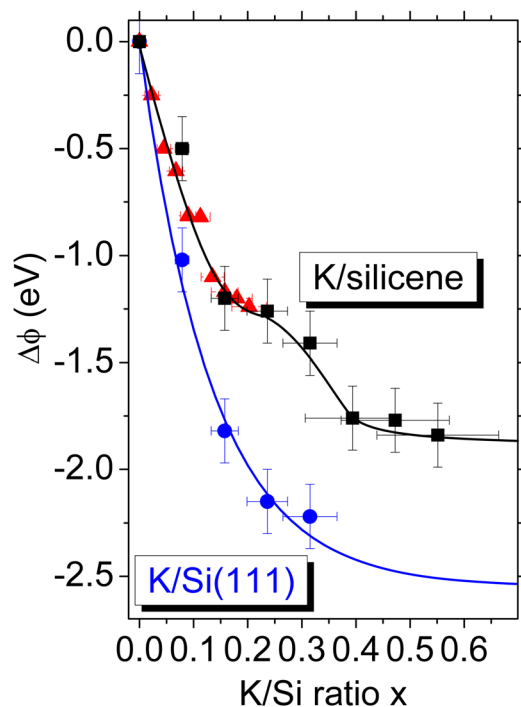


FIG. 1. Change of the work function, $\Delta\phi$, of the Si(111) (blue circles) and silicene/ZrB₂(0001) (black squares, red triangles) surfaces at room temperature with increasing potassium coverage, defined as the K/Si ratio x , as obtained at the NLS-BL U5UA (blue circles, black squares) and KEK-PF BL-18A (red triangles) set-ups.

Upon continuing exposure to potassium vapor, ϕ then drops again by another 0.3 eV followed by a very slow decrease. Since metallic potassium has a very low ϕ of about 2.24 eV,²³ it is expected that saturation shall only occur after a long deposition time upon which the surface is fully covered by a metallic potassium film.

In Figure 2, the x -dependent μ -LEED patterns are shown. The (2×2) pattern of pristine silicene on ZrB₂(0001) thin films shown in Fig. 2(a) is consistent with the reflection high-energy electron diffraction data reported previously,²¹ which corresponds to the $(\sqrt{3} \times \sqrt{3})$ -reconstruction of silicene.¹² The reconstruction of the surface does not change upon exposure to potassium atoms up to a level of $x = 0.16 \pm 0.03$, which indicates that the silicene layer remains structurally intact maintaining the epitaxial relation with the diboride surface. The variation of the intensity of the innermost $(\sqrt{3} \times \sqrt{3})$ -related LEED spots as a function of the kinetic energy of the electrons known as the LEED-IV curve (not shown) exhibits the same pattern and also the same intensities at energies above 200 eV. This may indicate that the degree of buckling does not change much upon K adsorption as theoretically predicted for free-standing, unreconstructed silicene.¹⁵

ARPES spectra obtained along the $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ direction in the vicinity of the $\bar{\Gamma}$ point of the repeated Brillouin zone (BZ) of the (2×2) -reconstructed ZrB₂(0001) surface are shown in Figure 3 as a function of the in-plane wave number k_{\parallel} . For pristine silicene ($x = 0$, Fig. 3(a)), an intense feature previously denoted “ X_2 ” approaches E_F by up to 250 meV at the K_{Si} point of unreconstructed silicene and has been assigned to a band derived from the π orbitals.¹² In the present measurements using the photon energy of $h\nu = 43$ eV, a

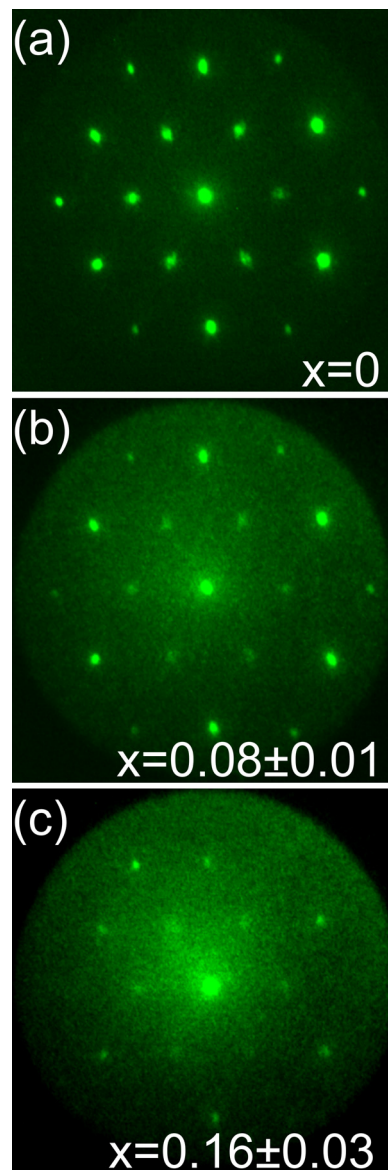


FIG. 2. μ -LEED patterns recorded at 30 eV, corresponding to the K atom coverage of: (a) $x = 0$; (b) $x = 0.08 \pm 0.01$; and (c) $x = 0.16 \pm 0.03$.

second, stronger dispersing feature denoted “ X_3 ” becomes visible. The presence of two upwards-curved π -electronic features is consistent with the prediction for two π bands in $(\sqrt{3} \times \sqrt{3})$ -reconstructed silicene.¹² As shown in Fig. 3(b) for $x = 0.18 \pm 0.03$, upon deposition of K atoms, the two π bands shift towards higher binding energy. For $x = 0.18 \pm 0.03$, this shift amounts to about 100 meV.

Note that the reconstruction of silicene leads to a direct electronic gap at the $\bar{\Gamma}$ point resulting from the back-folding of π bands into the reduced Brillouin zone.¹² Accordingly, as shown in Fig. 4(a) for pristine silicene, features X_2 and X_3 are mirrored as X'_2 and X'_3 within the 1st BZ. Two surface states denoted “ S_1 ” and “ S_2 ” are characteristic of the Zr-terminated ZrB₂ single crystal.^{21,24,25} The downwards-curved feature “ S_1 ,” in particular, appears to be parabolic in the vicinity of the \bar{M} point and originates from Zr 4d, 5s, and 5p orbitals of the outermost Zr layer.²⁴ Using the photon energy higher than in the previous experiments, a new upwards-curved, parabolic feature denoted “ X_4 ” can now be resolved around the \bar{M} point. The top of this

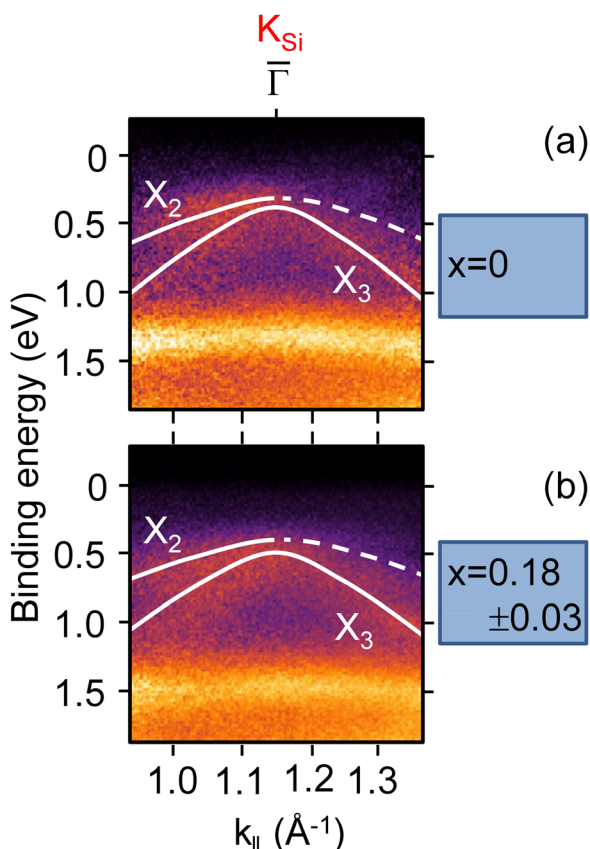


FIG. 3. Valence electronic structure of epitaxial silicene on $\text{ZrB}_2(0001)$ along the $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ direction, in the vicinity of the $\bar{\Gamma}$ point of the repeated BZ: (a) ARPES spectra of pristine silicene ($x=0$); and (b) at a K/Si ratio of $x=0.18 \pm 0.03$.

band at a binding energy of about 1.2 eV is by 0.5 eV well separated from the bottom of S_1 . In the other high-symmetry direction, along $\bar{\Gamma} - \bar{K} - \bar{M}$, there are a number of bands that are derived from both the bulk and surface of zirconium diboride that cannot easily be assigned at the present stage.

In Figs. 4(b) and 4(c), the ARPES spectra are shown at K/Si ratios of $x=0.09 \pm 0.01$ and $x=0.18 \pm 0.03$, respectively. Upon deposition of K atoms, a number of changes to the electronic structure can be recognized. First, a new band denoted “ X_5 ” appears at E_F right at the \bar{M} point. This electron pocket is certainly formed by electron donation from the alkali metal atoms to a formerly unoccupied band. It is plausible that this band is spatially localized within the surface region since charge transfer is stabilized by the presence of the K counter ions. The appearance of this new feature at the \bar{M} point of the $(\sqrt{3} \times \sqrt{3})$ -reconstructed silicene surprises, if one considers that free-standing, unreconstructed silicene,¹⁻³ like graphene,^{17,18} is predicted to display cone-like π^* bands in the vicinity of the K_{Si} point. This point corresponds to the $\bar{\Gamma}$ point and not to the \bar{M} point of $(\sqrt{3} \times \sqrt{3})$ -reconstructed silicene. However, for a particular buckling of free-standing, $(\sqrt{3} \times \sqrt{3})$ -reconstructed silicene, one of the π^* bands has been calculated to be rather flat in this crystallographic direction and also within about 300 meV from E_F .¹² Feature “ X_5 ” may derive from that band or may form as a hybrid with substrate electronic states.

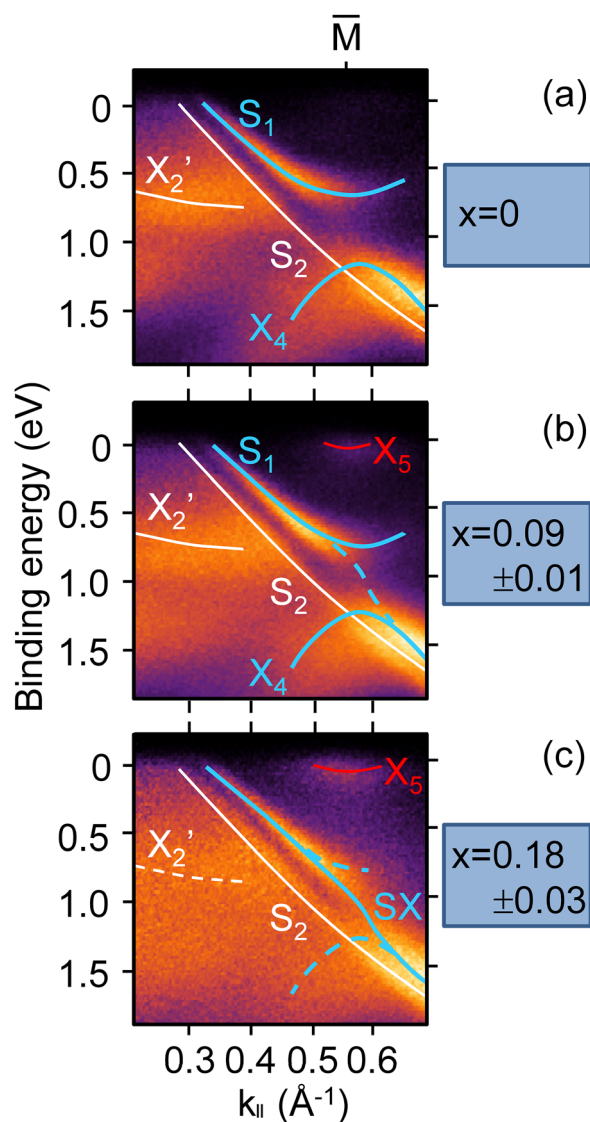


FIG. 4. ARPES spectra of epitaxial silicene on $\text{ZrB}_2(0001)$ along the $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ direction, in the vicinity of the \bar{M} point of the 1st BZ: (a) at $x=0$; (b) $x=0.09 \pm 0.01$; and (c) $x=0.18 \pm 0.03$.

The crossing point of S_1 with E_F does not change during deposition of K atoms such that it may be considered that this surface state does not accommodate additional electrons. This may indicate that charge transfer from the potassium atoms to Zr-derived orbitals may be minor. Instead, with increasing x , the high-binding energy part of S_1 straightens out and starts to merge with the upper part of X_4 forming a new band at $x=0.18 \pm 0.03$. This new feature is denoted “SX” in Fig. 4(b). The formation of such a hybrid band is consistent with stronger interactions between Si and Zr atoms characterized by an increasing hybridization between Zr $4d$ and silicene π orbitals. Since there are no other obvious orbitals to hybridize with, feature X_4 of pristine silicene may then also be assigned to one of the lower branches of the back-folded bands with possibly predominant π character.

On the other hand, for pristine silicene, the results show that hybridization between electronic states derived from silicene and from the ZrB_2 surface, at least for states along the $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ direction, may indeed be rather weak.

The identification of silicene-derived π bands allows the estimation of the overall occupied π band width in silicene to be about 2.5–3.0 eV, which is about a third of that in graphene and slightly smaller than that predicted for free-standing silicene.^{1–3} Note that the assignment of strongly dispersing states to π bands reported for silicon structures on Ag(111)¹⁰ is in contradiction with the relatively small total band width found in the present work.

In conclusion, the data presented here are consistent with a π -electronic system in $(\sqrt{3} \times \sqrt{3})$ -reconstructed, epitaxial silicene on the metallic diboride surface and a rather small degree of hybridization with d orbitals of the substrate in the pristine case. This in turn verifies our previous, yet preliminary, interpretation of the electronic structure.¹²

Upon adsorption of potassium atoms, distinct changes of the low-energy electronic structure of silicene on thin ZrB₂ films have been observed. In particular, electron donation to the silicene sheet results in the occupation of a formerly unoccupied (likely to be π^* -derived) state, a shift of π -electronic states towards higher binding energy and increasing hybridization between Zr $4d$ - and Si π -derived electronic states. If electron donation results in stronger interactions at the interface, it is expected that electron withdrawal by acceptors, e.g., iodine molecules, may lead to the opposite. With the synthesis of free-standing silicene remaining a major challenge, the tuning of electronic properties of epitaxial silicene with foreign atoms then promises an alternative way to realize the exciting properties predicted for free-standing silicene.

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